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EXCITED STATE COMPLEXES FROM LASER FLASH PHOTOLYSIS OF CYANOCUPRATE(I) SYSTEMS

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The three cyanocuprate(I) complexes, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$, are shown to photoeject hydrated electrons when excited in aqueous solution by 266-nm laser pulses of 7-ns duration. The three systems eject electrons at about the same high efficiency and experiments show that ionic strength of the solution has a strong influence on this efficiency. The quantum yields for electron ejection are higher in 2M ionic strength than in 1M ionic strength. Aside from the hydrated electron ejection, two transient intermediates, absorbing at 460 nm and 340 nm, respectively, are observed to form consecutively after excitation in solutions of $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$, but not in $Cu(CN)_4^{3-}$. These intermediates seem to be formed through bimolecular reactions with ground-state copper(I) in these solutions. The photoprocesses observed are all monophotonic, meaning that they occur by absorption of a single photon of light. A mechanism is proposed that suggests that the intermediates formed are of an excited dinuclear, or dimer, nature, and are thus called excimers.